PRELIMINARY ANALYSIS CONCERNING A MODEL FOR THE DETERMINATION OF ELEMENTS SPECIATION IN NATURAL WATERS

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The paper gives an introduction to the theoretical problems which substantiate the determination of the equilibrium speciation of dissolved components in natural waters. A new genuine model for calculating the activities of the chemical species to be found in low mineralized waters is presented. The calculation programme meant to this purpose gives, in this primary stage, full information on the activities of 157 species in solution as well as on the stability degree of 68 mineral species. The veracity of the proposed model is proved by comparing its results with the data given by other similar programmes processed in the same set of analytical measurements. This proves that the model acts correctly for the large majority of water constituents.

1. INTRODUCTION

The main types of chemical species to be found in natural waters are the free ions and the ionic associations. The concept of ions association was introduced in chemistry by Bjerrum, in 1926, in order to complete the Debye-Hückel theory concerning the electrolytes solutions. This concept was used in a remarkable way by G a r r e l s et al. (1961) who explain the extremely small values shown by the activity coefficient of the carbonate ion (CO_3^{--}) in sea water.

There are two types of associated ionic species : ion pairs and complexes. By ion pairs is generally meant the association having an essentially electrostatic bonding between the ions with the opposite charge. As far as the complexes are concerned the link forces contributing to the stability of the species are of a covalent type. The anions and the organic substances to be found in natural waters act as ligands. The metals characterised by an electronic configuration which is completed in s type orbitals, form with the ligands ion pairs. The metals of p type, belonging to the main groups of the periodical system, and of d type, the transitional metals, form both ion pairs and complexes (P e t r u c c i, 1971). Depending of the ligand nature the distinction between the anorganic and organic complexes is evident. In the first case the ligand is an anion as, for instance : carbonate (CO_3^{--}), sulphate (SO_4^{--}), chloride (Cl^-), fluoride (F^-), hydroxyl (OH^-) a.s.o., in the second one, the role of the ligand is played by an organic molecule.

By eliminating from the total of elements the inert gases, the synthetic elements or the products of the radioactive disintegration, as well as the few elements unidentified up to now, T u r n e r et al. (1981) conclude that the speciation of 71 elements is to be considered in natural waters. From these, 13 are considered the main water components (H, Na, K, Mg, Ca, Sr, B, C, O, S, F, Cl and Br), and the other 58 are trace elements. Taking into account that between the major components there are s type elements, respective alkaline and alkaline earth metals, it follows that the ion pairs have a more important share from the two types

Trav. Inst. Spéol. « Émile Racovitza », t. XXXI, p. 171—184, Bucarest, 1992

of ionic associations. On the other side, the complexing effect of the elements in traces, cannot be underestimated, because of their very strong tendency to associate, thus blocking a great part of the ligands concentrations. At the same time, the equilibria of hydrolysis are very competitive, process which is to be treated too in the frame of elements speciation.

The general calculating equations of the chemical equilibrium in multi component systems are well known but the ways of solving them and of drawing a coeherent and veridical program of calculations are practically infinite. In the topic literature many variants and calculus scheme are known, more or less extensive, with a wider or smaller applicability: van Breemen (1973), Thrailkill (1976), Wilcock (1976), Merino (1979), Morel (1983), a.s.o..

In this paper we give a method for determining the distribution of species in natural low mineralized waters, together with some of its results. The veridicity of the proposed model is proved by the comparison between the data found by applying this method with the data issued from other similar programs, carried out on the same set of chemical analysis of water.

2. THE CALCULATION OF THE SPECIATION

According to the Stumm and Brauner (1975) the method for determining the distribution of species relies on the principle that the total free energy of the system reaches a minimum at the equilibrium. This total free energy is the sum of the contributions of each of the existing chemical species in the system. This contribution depends on its standard free energy of formation, on its activity as well as on system temperature and pressure. There are two possibilities for calculating the speciation : the first consists in minimizing the Gibbs function of free energy, while maintaining a carefully correct masses' balance. Though direct, this method is less used due to the insufficient thermodynamic data available. The second method consists in a solution of the set of non-linear equations based on the mass action law and the mole balance equations.

The chemical analysis shows the data concerning the composition of natural waters, generally as concentrations. On the other side, the equations of calculus used for determining the speciation, rely on the thermodynamic principles, so that the constituents of the systems are characterised by their activities. The activity of a species depends on the whole interactions of the respective species within the system it belongs to. Consequently, for a correct calculus of activities, all the components and all the possible equilibria of the respective system should be taken into account.

As far as the speciation calculus is concerned, the thermodynamic constants peculiar to the equilibria of species formation have a decisive importance. There is a rich literature regarding the determination of these values, by means of a great diversity of methods. A first and comprehensive review of technical procedures is due to Nancollas (1966). Apart

from equilibrium constants, there other parameters which require permanent theoretical reevaluations and experimental investigations. Thus, one of the most difficult problem, is the determination of the activity coefficients belonging to the species are neutral from an electric point of view. In this view the Debye-Hückel theory is not sufficient, so that it was necessary to resort to a series of empirical formula of calculus.

The model of computations carried out by us has for a main object the determination of the activity of chemical species present at the equilibrium in natural waters. In this view, there were earlier studies such as the estimation of the speciation characterising the main components of karstic waters (M a r i n, 1979), by means of a calculus pattern similar to that of G a r r e l s and T h o m p s o n (1962). The present program takes into account the speciation of 22 elements and calculate the activity of 157 species in solution. Besides, as direct application, the evaluation of 68 mineral species stability towards the studied water sample.

The input data of the program are represented by the concentrations analytically determined, pH and temperature measurements as well as by the values of the equilibrium constants taken into account. The calculus pattern entails the following stages:

— establishing an initial ionic strength on the basis of analytic data, and calculating with it the activity of the ions considered totally free at the beginning;

— using the low of mass action as applied to the equilibrium reactions, the activity of ionic association is calculated with the free ions activities;

— all the activities determined by this way are reconverted in concentrations and introduced in masses balance equations;

— By means of contribution values acquired, a new ionic strength of the solution is calculated. Its value replaces the one from the initial stage, taking again the sequence of the calculus stages from the beginning. A number of iterations is carried out, so that the difference between two successive values of the ionic strenght should be at the limit of the least analytic error.

The species having as ligand the anions resulting from weak acids (H_3BO_3, H_2CO_3, H_4SiO_4, H_3PO_4 and H_2S) are treated differently from the ion pairs with the anions of strong acids (HNO_3, H_2SO_4 and halogen hydrides). In the first case the acids ionisation equilibria are initially calculated, considering the analytic concentration as the sum of all the molalities belonging to the respective species. Afterwards, the activity of the ionic association is estimated. In the second case, the analytical concentration of the anions coming from the strong acids are initially considered as total concentrations. On their basis, the activities of the ion pairs are determined, then the calculus is reiterated until the sum of respective species concentrations becomes equal to the concentration of the anion, as it was analytically determined.

The values of the equilibrium constants used by us have the program WATEQ (T r u e s d e l l a n d J o n e s, 1974) as a main source, excepting: species of boric acid by R e a r d o n (1976), hydratation of CO_2 and the dissociation of H_2CO_3 by H a r n e d and D a v i e s (1943) and H a r n e d and S c h o l e s (1941), carbonatic species of calcium and magne-

sium by Jacobson and Langmuir (1974), Reardon and Langmuir (1974) and Reardon (1975 a), species of the silicic acid and the associations with the anions of phosphoric acid by Turner et al. (1981), dissociation of H_3PO_4 and the ionic product of water by Robinson and Stokes (1959), ion pairs with SO_4^{--} by Reardon (1975 b), products of solubility for calcite and dolomite by Jacobson and Langmuir (1974), respectively by Langmuir (1971).

The values of 27 from 203 equilibrium constants used in the program are calculated depending on the temperature of water at the moment of sampling. In the other situation there were used the non-corrected values at 25°C. The activity coefficients are calculated by extended Debye-Hückel expression (Garrels and Christ, 1965) and for neutral ion pairs they were considered equals to unity, with two exceptions. For the ion pairs $CaSO_4^0$ and $MgCO_3^0$ the activity coefficients were calculated depending on the ionic strength by means of Reardon and Langmuir (1976) equations. The stability of minerals towards water is estimated by means of the saturation index defined as the logarithm of the ratio between the ion activity product for the mineral and the thermodynamic solubility product constant. For writing the calculus program the SYMPHONY (1.1.) processor was used.

3. RESULTS

The program we propose is only applicable to low mineralized waters. The calculation of the activity coefficients is made with Debye-Hückel equation, which is adequate only to the solutions with ionic strength smaller than 0.1 M (Stumm and Morgan, 1970). For showing the result of this model, a set of analytical determinations we processed, as proposed by Nordstom et al. (1979), characteristic to the continen-

Table 1

River Water test case data, in mg/l (After Nordstrom et al., 1979)

T = 9.5 grd. C			pH = 8.01
Density = 1.00 g/cm³			Eh = 0.44 V
DO = 10.94,	H2S = 0.002,		CO2 = 2.5
Na	=12.0	B	= 0.050
K	= 1.4	HCO3—1	=75.2
Mg	= 7.5	Si	= 8.52
Ca	= 8.52	NO2	= 0.019
Al	= 0.005	NO3	= 0.898
Fe+2	= 0.015	PO4	= 0.210
Mn	= 0.0044	SO4	= 7.7
Zn	= 0.00049	F	= 0.1
NH4	= 0.144	Cl	= 9.9
		Br	= 0.006
		I	= 0.0018

tal waters with weak ionic strength, which was generically called by its authors "River Water — test case". This set of chemical analysis is shown in Table 1. From the original data only the components processed by our program were hold.

The results of this calculus were shown in a diagram form, in this way the proportions between various species existing in a natural water may be more conspicuously pointed out. Thus, Figs. 1—4 show the concentration ratio diagrams for major cations, i.e.: Na^+, K^+, Mg^{++} and Ca^{++}, calculated for River Water test case, as a function of pH. In the diagrams there are plotted the molal concentrations, symbolising through the logarithm of the respective molality with a changed sign. Me^s represents the concentration of the ionic association with the respective metal. Table 2 shows the real share of the free ions, the calculations being realised for the same test case, and for a chemical analysis of karstic water, as reported by P i t m a n (1978). It is to be mentioned that the values found by him were acquired by applying the Garrels & Thompson model for calculating the speciation.

Table 2

Comparison of the percentage of free ions, saturation indexes and partial pressure of CO2

Ions	This study	Pitman (1978)	
		Reported	Values calculated using this program
Na+1	99.92	—	99.89
K+1	99.88	—	99.77
Mg+2	98.33	96.9	97.06
Ca+2	98.24	96.3	96.73
HCO3—1	98.89	97.1	98.00
SO4—2	93.78	85.3	85.03
Cl—1	100.00	—	100.00
pH	8.01	7.88	7.88
SI calcite	—0.766	+0.36	+0.097
SI dolomite	—1.640	+0,17	—0.480
—Log PCO2	3.22	2.65	2.64
Ionic Strength	0.00241	0.00457	0.00462

4. DISCUSSION

The veracity of the models, trying to describe the behaviour of natural systems, may only be tested experimentally. The direct measurement of physical or compositional parameters of the respective system is the only method to show the degree in which the proposed model reproduces the real situations. Unfortunately, we have no possibility to test experimentally our model. Nevertheless for checking in a way our calculus program, we compared the result acquired, by means of it, with the data given by similar programs. In this connection we were really helped by the work of N o r d s t r o m et al. (1979). They use two series of che-

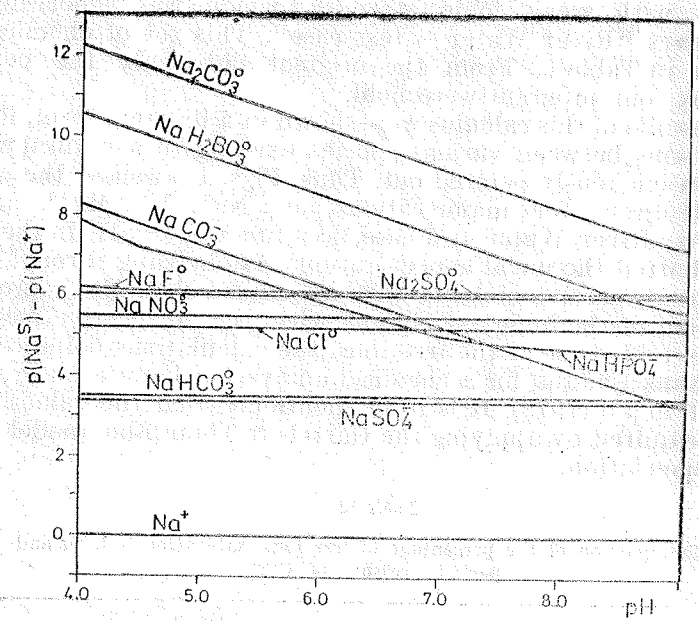

Fig. 1 — Equilibrium distribution of natrium species as a function of pH for „River Water" test case.

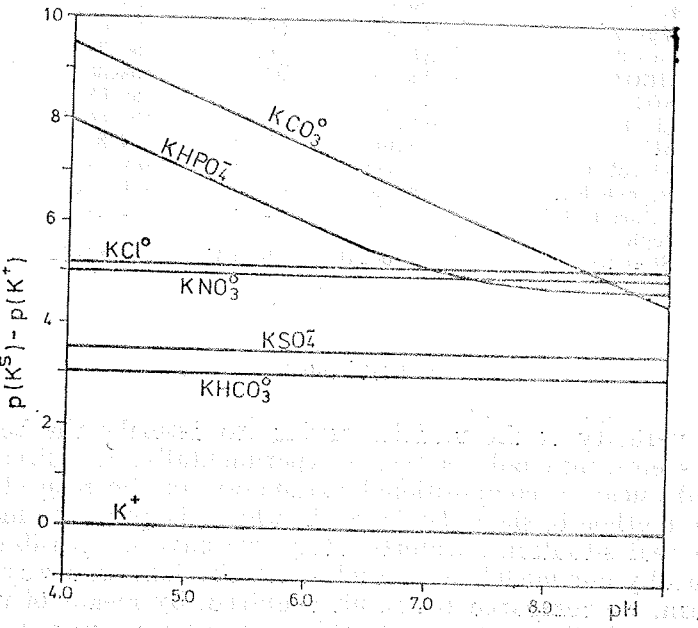

Fig. 2 — Equilibrium distribution of potassium species as a function of pH for „River Water" test case.

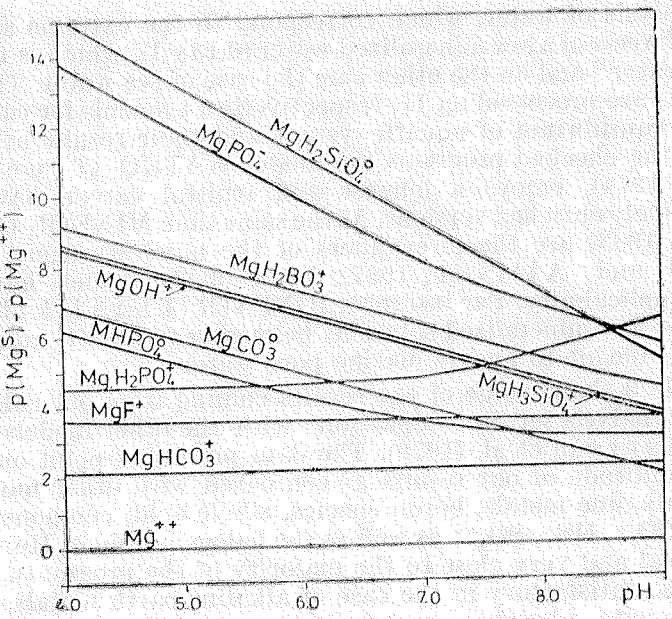

Fig. 3 — Equilibrium distribution of magnesium species as a function of pH for River Water" test case.

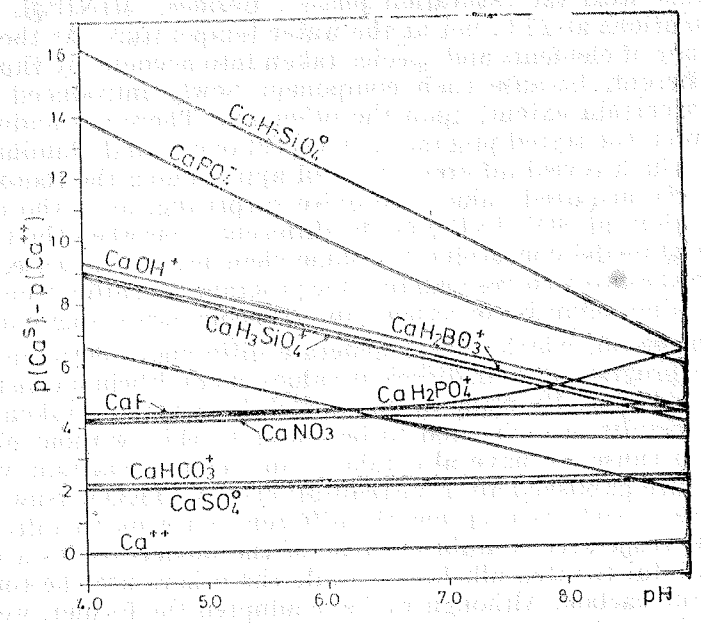

Fig. 4 — Equilibriu m distribution of calcium species as a function of pH for ,River Water" test case.

mical analysis of water, which correspond to the extreme situations, on one side the cese of a low mineralized water (0.13 g/l), which is equivalent to „River Water" and on the other side the case of sea water. The two series of analysis are processed on 11, respectivelly 14 models for calculating the chemical equilibrium of aquatic system, and their results are compared. Between the checked programs the model WATEQ (Truesdell and Jones, 1974), enjoys a longest and fruitful career, having a series of successively enriched versions. At the same time MINEQL and REDEQL (Morel, 1983) are the forerunners of the much stronger, MINTEQAI (Brown and Allison, 1987). Some of the models have a limited areas of applicability. For instance, IONPAIR (Thrailkill, 1976) was written for low mineralized solutions belonging to karstic aquifers, MIRE which was meant to anoxic marine pore waters.

Table 3 shows some of the results coming from our calculations on the given analysis set, in comparison with the other models to be found in Nordstrom et al. (1979). The data presented point out an almost perfect similitude of our results as compared with other models concerning the alkaline metals, boron species, silicic acid, components with nitrogen, HCO_3^-, HS^-, SO_4^{--} as well as the halogens anions. Here our results are identical and very close to the majority of the programs. The conformity is also satisfactory in the case of alkaline earth metals, manganese, zinc, carbonate, phosphats and hydrogen sulphide, were the deviations are of about 0.1—0.2 p(m).

We have to mention that there is no unanimity of views between the compared models. Some of the differences are explainabe, thus MINEQL and REDEQL calculate the speciation, so that the solution is in equilibrium with the saturation phases. Besides, MINEQL carried out the calculations at 25°C, not at the water temperature. At the same time, the number of elements and species taken into account by thus models, is not indifferent, because each component newly introduced in calculus acts, to a certain extent, upon the other too. There are main discrepancies between the tested programs, in respect to iron and aluminium concentrations, which reveal different ways of approaching the redox equilibria. Some of the acquired values are quite surprising, as is the case of iron concentrations at SOLMNEQ or the differences between the two variants of WATEQ model concerning the same element. In our case, the results we acquired for iron correspond to some programs and differ from the others. As far as aluminium is concerned, an erroneous processing is obvious.

The reason, which always generate differences between the results of various programs, lies in different values of equilibrium constants introduced in calculus. By using in our model the constants taken from WATEQ the results are expected to be closer to this, without attaining an identity, because we have also taken some of the constant values from the literature published after the realisation of WATEQ version used by us. In the case of carbonatic species the differences are due to a diverse approach to the respective equilibria. Some of the models use as a main input data, the total titrated alkalinity, while the others use the total content of anorganic carbon. Although we have adopted the former, we still think that in this matter, only laboratory experiment may show which is the objective process to be followed.

Table 3

p(m) of selected major species in River Water test case

(Values calculated with this program and reported by Nordstrom et al., 1979)

Program	This study	EQUIL	EQ3	ION PAIR	MINEQL 2	MIRE	REDEQL 2	SOLMNEQ	WATEQF	WATEQ 2	WATSPEC
Na+1	3.283	3.283	3.282	3.283	3.28	3.284	3.28	3.283	3.283	3.283	3.283
NaSO4−1	6.678	6.447	6.819	7.000	6.82	7.280	6.82	6.617	6.819	6.820	6.793
NaHCO3 aq	6.756	6.505	—	—	—	6.500	—	6.496	6.495	6.496	6.494
K+1	4.447	4.446	4.446	4.450	4.454	4.444	4.45	4.446	4.446	4.446	4.446
KSO4−1	7.957	7.830	7.896	—	7.59	7.819	7.60	7.902	7.935	7.936	7.910
Mg+2	3.518	3.523	3.519	3.518	3.53	3.523	3.53	3.519	3.519	3.519	3.520
MgSO4 aq	5.666	5.586	5.750	5.700	5.47	5.593	5.45	5.726	5.767	5.756	5.600
MgHCO3+1	5.652	5.636	5.491	5.600	5.16	5.568	5.25	6.027	5.495	5.496	5.486
MgCO3 aq	6.375	5.470	6.133	6.000	5.55	5.988	5.65	5.622	6.156	6.157	6.147
Ca+2	3.524	3.532	3.529	3.522	3.540	3.530	3.539	3.527	3.525	3.525	3.525
CaSO4 aq	5.586	5.537	5.578	5.600	5.58	5.533	5.58	5.545	5.578	5.577	5.545
CaHCO3+1	5.724	5.288	5.343	—	5.17	5.409	5.27	5.518	5.722	5.723	5.714
CaCO3 aq	6.131	5.681	5.933	6.000	5.76	5.732	5.27	5.959	6.000	6.001	5.992
Fe+2	6.638	6.711	6.639	—	15.18	6.896	15.18	8.389	12.167	6.579	11.953
FeOH+1	8.194	7.057	7.428	—	15.82	6.855	15.83	26.711	14.257	8.669	13.860
Mn+2	7.114	7.100	8.205	—	7.14	7.138	7.13	7.099	7.119	7.119	—
MnOH+1	9.761	—	11.403	—	9.28	9.804	9.28	—	10.264	10.347	—
MnSO4 aq	9.158	9.166	10.383	—	9.18	9.213	9.18	9.289	9.864	9.864	—
Zn+2	8.262	8.131	8.129	—	8.15	—	8.48	7.129	—	8.504	—
ZnCO3 aq	9.158	—	—	—	—	—	8.51	—	—	8.720	—
H3BO3 aq	5.354	5.364	—	—	5.37	—	—	5.379	5.354	5.355	5.355
H2BO3−1	6.716	6.570	—	—	6.41	—	6.42	6.726	6.690	6.711	6.688
HCO3−1	2.918	2.924	2.920	2.915	2.93	2.919	2.93	2.918	2.917	2.917	2.917
CO3−2	5.465	5.164	5.346	5.300	5.01	5.168	5.12	5.328	5.334	5.333	5.333
H4SiO4 aq	3.520	3.528	—	—	3.53	—	3.53	3.523	3.851	3.520	3.520
H3SiO4−1	5.792	—	—	—	—	—	—	—	—	—	—
H2SiO4−2	10.581	—	—	—	—	—	—	—	—	—	—

Table 3 (continuare)

NH4+1	5.122	5.098	—	—	5.14	—	5.13	5.105	5.106	5.106	10.392
NO3—1	4.839	4.839	—	4.84	—	—	—	4.839	4.839	4.839	4.839
H2PO4—1	6.539	5.694	—	—	7.78	6.654	8.06	6.622	6.625	6.625	—
HPO4—2	5.803	5.818	—	—	7.07	5.773	7.16	5.813	5.793	5.793	—
PO4—3	13.002	10.030	—	—	11.41	—	11.40	10.189	10.156	10.156	—
H2S aq	8.146	—	8.076	—	—	—	—	8.071	8.146	8.403	8.146
HS—1	7.288	—	7.268	—	—	—	—	7.299	7.288	7.544	7.288
S—2	12.128	—	17.140	—	—	—	—	16.489	12.613	12.870	12.615
SO4—2	4.124	4.129	4.122	4.120	4.14	4.128	4.14	4.122	4.121	4.121	4.164
F—1	5.287	5.281	—	—	5.29	—	5.29	5.282	5.284	5.284	—
Cl—1	3.554	3.401	3.554	3.554	3.55	3.556	3.55	3.558	3.554	3.554	3.554
Br—1	7.124	—	—	—	7.12	—	7.12	—	7.124	7.124	7.120
I—1	7.848	—	—	—	7.785	—	7.86	—	—	—	—
Ionic Strength	0.00241	0.00238	0.00239	0.00240	0.00300	0.00240	0.00300	0.00240	0.00240	0.00241	0.00239

Table 4

Saturation Index for selected minerals in River Water test case
(Values calculated with this program and reported by Nordstrom et al., 1979)

Mineral	Formula	This study	EQUIL	EQ3	ION PAIR	MIRE	SOLMNEQ	WATEQF	WATEQ 2	WATSPEC
Calcite	CaCO3	−0.766	−0.51	−0.585	−0.673	−0.461	−0.765	−0.634	−0.634	−0.63
Dolomite	CaMg(CO3)2	−1.640	−0.73	−0.248	−1.340	−0.730	−1.329	−1.384	−1.386	−1.38
Siderite	FeCO3	−1.733	−1.37	+0.456	—	−2.329	−3.377	−7.347	−1.760	−7.13
Rhodochrosite	MnCO3	−2.349	−1.81	−3.225	—	−2.097	−2.136	−2.180	−2.180	—
Gypsum	CaSO4*2H2O	−2.981	−3.00	−2.962	—	−3.081	−2.942	−3.057	−2.969	−3.25
Hydroxyapatite	Ca5(PO4)3OH	+8.085	+2.82	—	—	+5.891	+5.046	−1.784	−1.722	—

Table 4 (continuare)

Mineral	Formula	This study	EQUIL	EQ 3	IONPAIR	MIRE	SOLMNEQ	WATEQF	WATEQ 2	WATSPEQ
Fluorite	CaF2	−5.188	−4.39	—	—	—	−3.338	−3.079	−3.074	—
Ferric Hydrox. Am.	Fe(OH)3	+4.957	—	—	—	—	−7.584	+1.304	—	—
Goethite	FeO(OH)	+7.198	+5.59	—	—	—	−1.484	+7.810	+6.843	+5.06
Hematite	Fe2O3	+15.688	+8.11	+18.332	—	—	−3.252	+15.144	+13.223	+13.52
Chalcedony	SiO2	+0.003	—	+0.490	—	—	+0.217	−0.142	+0.189	—
Quartz	SiO2	+0.486	+0.47	+0.776	—	—	+0.697	+0.405	+0.736	+0.74
Sepiolite	Mg2SiO7. .5(OH)*3H2O	−4.124	−4.55	—	—	—	−5.734	−3.699	—	—
FeS Amorphous	FeS	−10.123	—	—	—	—	—	−7.644	−2.313	—
Mackinawite	FeS	−18.686	—	—	—	—	—	−6.928	−1.580	—

Table 4 gives the values of some saturation indexes for "River Water" towards some minerals. We recall that the saturation index is an empirical reference value, defined as the ratio between the product of the activities of the ions forming the respective mineral and its solubility product. As it is evident, the differences between the results of the diverse models are greater than the ones reported with the species concentrations. This could be explained firstly by the storing up of all calculus errors, concerning the individual ions activities, and secondly by using some different values for the solubility products.

Excepting the gibsite, the caolinite and the mackinawite, the values found by us join the frame of determination reported by the other models. At first two minerals, the differences were expected because of a wrong calculation of the aluminium ion activities. For the mackinawite we cannot give yet a satisfactory explanation. We think that generally the value range related to the programs checked is unacceptably wide. This is why we think that experimental examination is more necessary here, there is in other directions.

In comparison between the values acquired by us and the results found by means of other calculus programs is obviously not a sufficient modality of checking the proposed model. In the future, the correction of its errors is necessary as well as a general improvement of it.

5. CONCLUSIONS

This paper presents an attempt to determine the speciation of dissolved components found in equilibrium in natural waters. The calculation program, even being in an initial stage of aquirement, succeds in giving information about the activities of 157 species in solution, resulting from 22 elements and to valuate the stability degree of 68 mineral species. For checking the validity of the proposed model, the data obtained by using it, were confronted to the results reported by other authors, using similar calculus programs, by means of processing the same series of chemical analysis. The test was made in the case of a low mineralized water, with an ionic strength of 0.0025 M.

The elements included in this paper call for some conclusive statements, the theoretic aspects and the observations from the applicative part of the work are taken into account.

1. Any method of determining the speciation at the equilibrium of the components belonging to an aqueous solutions is based on analytical data, which describe the composition of the respective solution.

2. The relations used in the computation of speciation are given by the thermodynamics, particularly of the thermodynamics of electrolyte solutions, as well as by chemical kinetics, their concepts and specific measures being resorted to.

3. A model for describing rigorously the behaviour of water in natural conditions shall take into account on one side, a scale as wide as possible of processes liable to act upon the composition of water and, on the other side, to use the parameters which characterize correctly the respective phenomena. In this letter view, the values of the thermodyna-

mic, constants peculiar to chemical equilibria involved in the model, have a foremost importance.

4. The comparison of the concentration values and the saturation indexes of the minerals, as acquired by other authors (by means of various calculus programs for speciation) on test-case, shows a series of non-concordances between the reported figures, in some situations main discrepancies appearing. This calls for a detailed investigation of the chemical equilibrium in natural waters, concomitantly with experimental checkings of reference components.

5. The method for valuating the activities of chemical species, to be found in natural waters, as proposed by us, is applicable only to the low mineralized waters, in this starting phase of achievement.

6. The searching of the results obtained through our calculations comparatively with the data, found by other authors, on the analysis series "River Water", proves that, for the great majority of the components, the proposed model is correct.

REFERENCES

1987 BROWN D. S. and ALLISON J. D., *MINTEQA1, An equilibrium metal speciation model : User's manual;* U. S. Environmental Protection Agency, EPA/6003—87/012, 92p...

1961 GARRELS R. M., THOMPSON M. E. and SIEVER R., *Control of carbonate solubility by carbonate complexes.* Amer. J. Sci., **259** (1), pp. 24—45.

1962 GARRELS R. M. and THOMPSON M. E., *A chemical model for seawater at 25 C and one atmosphere total pressure.* Amer. J. Sci., **260** (1), pp. 57—66.

1965 GARRELS R. M. and CHRIST C. L., *Solutions Minerals and Equilibria.* Harper and Row. New York.

1941 HARNED H. S. and SCHOLES S. R., *The ionization constant of HCO3— 1 from 0 to 50 C.* J. Amer. Chem. Soc., **63** (9), pp. 1706—1709.

1943 HARNED H. S. and DAVIS R. Jr., *The ionization constant of carbonic acid in water and the solubility of carbon dioxide in water and aqueous solutions from 0 to 50 C.* J. Amer. Chem. Soc., **65** (10), pp. 2020—2027.

1974 JACOBSON R. L. and LANGMUIR D., *Dissociation constants of calcite and CaHCO3+ 1 from 0 to 50 C.* Geochim. Cosmochim. Acta, **38** (2), pp. 301—318.

1971 LANGMUIR D., *The geochemistry of some carbonate ground waters in central Pennsylvania.* Geochim. Cosmochim. Acta, **35** (10), pp. 1023—1045.

1979 MARIN C. *Ion pairs in karst waters.* Trav. Inst. Spéol. « Emile Racovitza » **18**, pp. 249—258.

1979 MERINO E., *Internal consistency of a water analysis and uncertainty of the calculated distribution of aqueous species at 25 C.* Geochim. Cosmochim. Acta, **43**, pp. 1533—1542.

1983 MOREL F. M. M., *Principles of Aquatic Chemistry.* John Wiley & Sons, New York, 446 pp.

1966 NANCOLLAS G. H., *Interactions in Electrolyte Solutions.* Elsevier, 180 pp.

1979 NORDSTROM D. K. et al., *A comparison of computerized chemical models for equilibrium calculations in aqueous systems ;* in E. A. Jenne edit. *Chemical Modeling in Aqueous Systems,* American Chemical Society Symp., Series 93, pp. 857—892.

1971 PETRUCCI S., *Statistical thermodynamics of ionic association and complexation in dilute solution of electrolytes ;* in S. Petrucci edit., *Ionic Interactions* Vol. 1, Academic Press, New York.

1978 PITMAN J. I., *Carbonate chemistry of groundwater from tropical tower karst in South Thailand.* Water Resour. Res., **14** (5), pp. 961—967.

1975 a REARDON E.J., *Thermodynamic properties of some sulfate, carbonate and bicarbonate ion pairs.* Dissertation Abstracts, 35 (11), Order No. 75—9830.

1975 b REARDON E. J., *Dissociation constants of some monovalent sulfate ion pairs at 25 C from stoichiometric activity coeficients.* J. Phys. Chem., **79**, pp 422—425.

1976 REARDON E.J., *Dissociation constants for alkali earth and sodium borate ion pairs from 10 to 50 C.* Chem. Geol., **18**, pp. 309—325.

1974 REARDON E. J. and LANGMUIR D., *Thermodynamic properties of the ion pairs MgCO3 (aq) and CaCO3 (aq) from 10 to 50 C.* Amer. J. Sci., 274 (6), pp. 599—612.
1976 REARDON E. J. and LANGMUIR D., *Activity coefficients of MgCO3 (aq) and CaSO4 (aq) ion pairs as a function of ionic strenght.* Geochim. Cosmochim. Acta, **40** (5), pp. 549—554.
1959 ROBINSON R. A. and STOKES R. H., *Electrolyte Solutions,* Butterworths Scientific Publications, London, 560 pp....
1970 STUMM W. and MORGAN J. J., *Aquatic Chemistry.* John Wiley & Sons, New York, 583 pp..
1975 STUMM W. and BRAUNER P. A., *Chemical speciation,* in J. P. Riley and G. Skirrow edits. *Chemichal Oceanography,* Vol. 1, pp. 173—239. Academic Press.
1976 THRAILKILL J., *Carbonate equilibria in karst waters ;* in V. Yevjevich ed., *Karst Hydrology and Water Resources,* Vol. 2 Karst Water Resources. Proc. U. S. — Yougoslavian Simp., Dubrovnik, 1975. Water Resources Publications. Fort Collins.
1974 TRUESDELL A. H. and JONES B. F., *WATEQ, a computer program for calculating chemical equilibria of natural waters.* Jour Res. U. S. Geol. Survey. **2** (2), pp. 233—248.
1981 TURNER D. R., WHITFIELD M. and DICKSON A. G., *The equilibrium speciation of dissolved components in freshwater and seawater at 25 C and 1 atm. pressure.* Geochim. Cosmochim. Acta, **45** (6), pp. 855—881.
1973 Van BREEMEN N., *Calculation of ionic activities in natural waters.* Geochim. Cosmochim. Acta, **37** (1), pp. 101—107.
1976 WILCOCK J. D., *The computer in speleology,* in T. D. Ford and C. H. D. Cullingford edits. *The Science of Speleology.* Academic Press, London.

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Received March 14, 1992